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(54) Title: COMPOSITION FOR CLEANING HARD SURFACES

(57) Abstract: The invention provides liquid abrasive cleaning compositions for hard surfaces which are clear aqueous liquid gels comprising one or more detergent surfactants and macroscopic abrasive particles which are dispersed through the liquid. The gel and the particles preferably have different colours. The particles preferably have fairly uniform particle diameters of between 0.3 and 2.5mm. The invention also provides a process for cleaning hard surfaces comprising the step of applying a composition according to the invention to the surface.

Composition for cleaning hard surfaces

5 Field of the invention

The present invention relates to liquid compositions for cleaning hard surfaces. Particularly, the invention relates to clear liquid cleaning gels containing macroscopic solid 10 particles.

Background to the invention

- 15 Liquid abrasive cleaning compositions for hard surfaces are well known in the art. They generally have a milky white appearance. They have sufficient viscosity at low shear stress to keep the fine abrasive particles evenly dispersed in the liquid, while at the same time they behave as true
- 20 liquids when being dispensed from a bottle. The fine abrasive particles (powder) in these compositions generally have a particle size below 200 micron, in most cases below 100 micron. Well know abrasives used in such compositions are silica, calcite, feldspar and similar inorganic
- 25 materials as well as several organic polymer particles, all with a Moh hardness of up to 6. Although many consumers extensively use such compositions, some do not appreciate the feel or appearance of these products, or fear that they might scratch their delicate surfaces.

Some liquid abrasive products on the market consist of a gel-like opaque liquid in which a variety of coarse and

fine irregularly shaped abrasive polymer particles are dispersed varying in diameter between more than 1 mm at one end and hardly visible to the naked eye at the other end. Because of this the total product appearance is

- 5 unattractive. Thus, there is a need for a new liquid hard surface cleaning product containing solid particles, which is visually appealing to the consumer and at the same time cleans effectively.
- 10 In the skin cleansing art products exist which are known as facial scrubs and which consist of a clear viscous liquid in which coarse abrasive particles are dispersed. Since such products are in intensive contact with the skin, they must have about neutral pH. They generally contain little
- 15 or no detergent surfactant and to the extend that they do, such surfactants are chosen from those which are skin-friendly and generally expensive. Such products are developed specifically for cleaning skin and are generally unsuitable for any other purpose, more specifically for
- 20 removing tough soil from hard surfaces.

In US 5,741,770 and in WO97/41204 liquid crystal cleaning compositions are disclosed which are transparent or slightly turbid and contain small amounts of abrasive

- 25 particles. The particles may be zeolites with a mean particle size of 8-10 μ m, amorphous silica with a particle size of up to 300 μ m or polyethylene powder with a particle size of up to 500 μ m
- 30 W000/65019 discloses liquid abrasive cleaning compositions containing a fine particulate abrasive and in addition thereto microcapsules containing various additional

components such as perfume, silicone oil and the like. In view of the specified amount and particle size of the abrasive, the compositions are clearly not transparent or translucent.

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- WO00/36078 discloses pourable transparent laundry detergent compositions, containing at least 15% surfactant. The compositions are thickened to be able to suspend macroscopic capsules containing ingredients that are
- 10 desirably kept separate from the concentrated and highly alkaline detergent solution. Similar compositions, also for other applications, are disclosed in GB 1303810. The capsules do not have abrasive properties.
- 15 Thus, although various liquid compositions containing suspended particles in a large variation of particle size and undisclosed shape are described in the prior art for various purposes and applications, methods and measures to increase the visual appearance of such compositions to the 20 consumer appear to have been neglected.

Brief description of the invention

25 The invention provides liquid cleaning compositions for hard surfaces which are clear aqueous liquid gels comprising one or more detergent surfactants and macroscopic abrasive particles, which are dispersed in a stable fashion through the liquid.

30

The invention further provides a process for cleaning hard surfaces comprising the step of applying to the surface a

clear aqueous liquid gel which comprises one or more detergent surfactants and macroscopic abrasive particles which are evenly dispersed through the liquid.

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Detailed description of the invention

All amount percentages mentioned herein are by weight and based on the total composition unless specifically indicated otherwise.

The cleaning compositions of the invention are clear aqueous liquid gels. Thus, all components of the compositions, with the exception of the abrasive particles, 15 are clearly soluble in water. The required viscosity to give the composition its gel consistency is obtained by the addition of suitable thickening agents that are able to give a clear solution. Such thickening agents are known in the art and suitable examples include various vegetable or 20 microbial polysaccharide gums, such as gum arabic, xanthan, alginates and the like, and synthetic polymers e.g. homopolymers of acrylic, methacrylic or maleic acid and copolymers thereof with each other and/or other monomers such as styrene, vinyl ethers etc. such as are marketed by 25 various manufacturers under tradenames such as ACUSOL, POLYGEL, CARBOPOL, RHEOVIS and similar products. For the purposes of this invention a gel is considered to be clear if it transmits at least 50% of light at any one wavelength in the visible region i.e. between 400 and 30 800nm, preferably 550-700nm, measured in a 1cm cuvette in the absence of dyes and abrasive particles. Preferably the

transmittance is at least 70%, more preferably at least 90%.

Gels which are satisfactory for the purposes of the present invention generally have a viscosity of between 100 and 1000 mPas, preferably at least 250 mPas, more preferably 300-750 mPas at 21 sec⁻¹ (measured with a Haake viscometer at 20°C). The low shear rate viscosity is such that the gel is able to suspend the macroscopic particles.

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In many liquid abrasive cleaning products known in the art the required viscosity is obtained by using self-thickening (structuring) mixtures of surfactants often in combination with electrolytes. Although some specific combinations of surfactants under specific circumstances have been disclosed to lead to a transparent or translucent liquid crystal structure, such thickening systems are generally unsuitable for the purposes of the present invention. Most structured surfactant systems cause the liquid to be 20 opaque.

Abrasive particles

25 In order for the cleaning compositions according to the invention to visually appeal to the consumer the particles are macroscopic, i.e. clearly visible separately to the naked eye. This is in contrast to most abrasive powder particles which generally have average particle size well 30 below 0.3mm and in the vast majority of cases at most 0.1mm (100µm).

Thus, the particles according to the invention have an average particle size between 0.3 and 2.5mm, preferably more than 0.5 and at most 1.5mm. Further, the visual appeal of the compositions is considerably enhanced if the 5 particles are of fairly uniform particle size i.e. they all have a particle size within the range of plus or minus 70% of the average particle size, preferably within a range of ± 50%, more preferably ± 30%.

- 10 The abrasive particles are used in an amount of at least 0.1%, preferably 0.5%. In order to retain the transparent character of the total composition the maximum amount of particles is 20%, preferably 10%, more preferably 5%.
- 15 The particles may be made of abrasive materials known in the art. Thus, they may consist of granules of one or more of the well known inorganic abrasives such as silica, silicates, calcite and the like. They may consist of polymer granules, such as polyethylene, polypropylene,
- 20 polycarbonate and the like. Particularly suitable are granules of a biodegradable polymer, such as the starch-derived plastics known in the art.

Alternatively, the abrasive particles may be made of softer 25 materials such as hard waxes and fats, hard fatty acids, hard fatty acid soaps and the like. Such materials may also be mixed with fine particles of any of the known abrasives or with other materials, preferably solid materials, suitable for improving the cleaning process and thereafter 30 formed into granules of the required size.

The visual appeal of the particles, and therefore the total composition, is further enhanced if the particles have a certain minimum sphericity, such that the ratio between the longest and the shortest diameter of a particle in any one 5 direction is at most 3:1, preferably at most 2:1 or even 1.5:1. Particularly preferred are particles with a round, preferably a smooth round shape. Such particles may be made by prilling processes involving making a melt of the particle material, converting it into droplets, which are 10 thereafter cooled in a gas (air) flow. Various processes and suitable equipment therefore are known in the art and may be applied to the organic abrasives, provided they are sufficiently low melting. High melting powders such as inorganic abrasive powders may be made into suitably shaped 15 particles by various agglomeration processes known in the art, if necessary using an aglomeration binder.

Although the cleaning compositions according to the invention may consist of a colourless liquid and solid 20 particles having their natural colour (in many cases white), the compositions are considerably more attractive to the consumer if the liquid and the particles have clearly different colours. They may have different shades of the same colour, e.g. dark blue particles in a light 25 blue liquid, or preferably, the liquid and the particles have contrasting colours e.g. white particles in a blue, green or yellow liquid or vice versa, or coloured particles in a differently coloured liquid.

30 The pH of the cleaning compositions may vary within wide limits and will generally be between 2 and 14. Certain surfaces are acid-sensitive and for those a composition

with pH of at least 3, preferably 3.5 or even 4 is advised. Improved cleaning of greasy soils is often obtained at alkaline pH i.e. above 7, preferably above 7.5. pH above 12 is generally not required.

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Surfactants

The compositions according to the invention comprise one or more surfactants which may be chosen from a wide range of 10 anionic, nonionic, cationic, amphoteric and zwitterionic surfactants, examples of which are given below.

A suitable class of anionic surfactants are water-soluble salts of organic sulphuric acid esters and sulphonic acids
15 having in the molecular structure an alkyl group containing
8-22 C atoms or an alkylaryl group containing 6-20 C atoms in the alkyl part.

Examples of such anionic surfactants are water-soluble salts 20 of:

- long chain (i.e. 8-22 C-atom) alcohol sulphates
 (hereinafter referred to as PAS), especially those
 obtained by sulphating the fatty alcohols produced by
 reducing the glycerides of tallow or coconut oil;
- 25 alkylbenzene-sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
 - secondary alkanesulphonates.

Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers
- of fatty alcohols derived from tallow and coconut oil;
 - fatty acid monoglyceride sulphates;

- sulphates of ethoxylated aliphatic alcohols containing
 1-8 ethyleneoxy units;
- alkylphenol ethyleneoxy-ether sulphates with from 1 to 8
 ethyleneoxy units per molecule and in which the alkyl
- 5 groups contain from 6 to 14 carbon atoms;
 - the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali.

A suitable class of nonionic surfactants can be broadly

10 described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkylaromatic in nature. The length of the hydrophilic or polyoxyalkylene chain that is attached to any particular

- 15 hydrophobic group can be readily adjusted to yield a watersoluble compound having the desired balance between
 hydrophilic and hydrophobic elements. This enables the choice
 of nonionic surfactants with the right HLB. Particular
 examples include:
- 20 the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol;
 - condensates of alkylphenols having C6-C15 alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol;
- condensates of the reaction product of ethylene-diamine
 30 and propylene oxide with ethylene oxide, the condensates
 containing from 40 to 80% of ethyleneoxy groups by

weight and having a molecular weight of from 5,000 to 11,000.

Other classes of nonionic surfactants are:

- 5 alkylglycosides, which are condensation products of long chain aliphatic alcohols and saccharides;
 - tertiary amine oxides of structure RRRNO, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon
- atoms, e.g. dimethyldodecylamine oxide;
 - tertiary phosphine oxides of structure RRRPO, where one R is an alkyl group of 8 to 20 carbon atoms and the other R's are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine
- 15 oxide;

30

- dialkyl sulphoxides of structure RRSO where one R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyl-tetradecyl sulphoxide;
- 20 fatty acid alkylolamides;
 - alkylene oxide condensates of fatty acid alkylolamides;
 - alkyl mercaptans.

Suitable amphoteric surfactants are derivatives of aliphatic 25 secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium N-2-hydroxy-dodecyl-N-methyltaurate.

Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl

groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium bromide.

- 5 Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for
- 10 instance 3-(N,N-dimethyl-N-hexadecylammonium)-propane-1-sulphonate betaine, 3-(dodecylmethyl-sulphonium)-propane-1-sulphonate betaine and 3-(cetylmethyl-phosphonium)-ethanesulphonate betaine.
- 15 Further examples of suitable surfactants are compounds commonly used as surface-active agents described in the well-known textbooks: "Surface Active Agents" Vol.1, by Schwartz & Perry, Interscience 1949, Vol.2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of
- 20 "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981.
- 25 Anionic and nonionic surfactants and combinations thereof are particularly preferred. In choosing the (combination of) surfactants care should be taken that they give a clear solution. Hydrotropes such as Na xylene- or cumenesulfonate or others known in the art may be added if 30 necessary.

The surfactants are generally present in an amount of at least 0.1%, but below 15%, preferably 0.5-10%, more preferably at least 1.0%.

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Optional components

The compositions according to the invention may contain various optional components well known in the art which 10 improve cleaning performance or consumer appeal. Thus, the compositions may contain builders, chelating agents, electrolytes, organic solvents, active halogen or peroxy bleaching agents, pH regulating agents, anti-foams, antimicrobials, preservatives, perfumes, insect repellents, 15 etc.

The process

- 20 The process for cleaning a hard surface involves applying to the hard surface a suitable amount of the composition according to the invention, generally followed by rubbing the composition over the surface to be cleaned using a wipe or cloth. The composition may be applied directly to the
- 25 surface or, alternatively, the composition may be applied to the (preferably damp) wipe or cloth first and thereafter this is rubbed over the surface with the side on which the composition was applied facing the surface. In case the abrasive particles are made of polymer or other relatively
- 30 soft material the compositions according to the invention are very suitable for cleaning delicate surfaces which would otherwise easily be scratched.



Example 1

A clear liquid blue coloured gel was prepared, according to 5 the formula below, which contained fatty acid granules having a diameter of 0.8 mm ± 20% dispersed therein.

INGREDIENT	TRADE NAME	SUPPLIER	LEVEL
			In %
Phosphoric Acid			0.050
Nonionic	Neodol 91.8	Condea DAC	3.000
Polymer	Carbopol 2623	Goodrich	0.280
Silicon	DB31		0.003
Nonionic	Neodol 91.5	Condea DAC	2.000
Sodium bicarbonate	Baking Soda	Solvay	0.100
Preservative	Proxel GXL	Zeneca	0.020
Fatty acid granule	Simiol 60	Uniqema	1.000
NaOH to pH 8.0		•	0.110
Perfume			0.270
Blue colourant	Blu Patent	Fiori	0.0006
Demin water		to	100

10 Example 2

A clear liquid green coloured gel was prepared, according to the formula below, which contained polyethylene granules having a diameter of 0.8 mm \pm 20% dispersed therein.

15 The product had a viscosity of 380 mPas at 21 sec⁻¹ and 20°C and a pH of 11.

INGREDIENT	TRADE NAME	LEVEL in %
·		
Xanthan gum	Kelzan ST	0.50
Diphosphonic acid	Dequest 2010	0.75
NaOH		1.20
Nonionic C12-C15 7EO	Dobanol 23 6.5	3.30
LAS acid		1.72
Di-ethylene glycol mono-butyl	Butyl Digol	2,00
ether		,
Fatty acid	Prifac 7907	0.09
Colourant	Blu Patent V	
Perfume		0.50
Polyethylene granules	AC 316	1.00
Demin water	to	100.

Example 3

- A mildly acidic (pH around 4.5) hydrogen peroxide containing clear hard surface cleaning gel was prepared according to the formula below. Fatty acid prills containing 10% by weight (calculated on the prills) sodium to bicarbonate and having a diameter of 1.0 mm + 20% were
- 10 bicarbonate and having a diameter of 1.0 mm \pm 20% were dispersed therein.



INGREDIENT	TRADE NAME	LEVEL in %
Sequestrant	Dequest 2046	0.10
Nonionic	Lialet 111-5.5EO	2.00
	Dobanol 91 8EO	5.00
Fatty acid (in solution)		0.30
Polyacrylate polymer	Carbopol ETD2623	0.30
Hydrogen peroxide		3.00
Citric acid		0.08
Sodium hydroxide	(buffer)	as required
Dye		
Perfume		
Fatty acid prills	·	2.0

CLAIMS

- Liquid abrasive hard surface cleaning composition comprising one or more detergent surfactants characterised in that it is a clear aqueous gel comprising macroscopic abrasive particles dispersed in the liquid which have an average particle size between 0.3 and 2.5mm.
- Cleaning composition according to claim 1 characterised in that the particle size is more than 0.5mm
- 3. Cleaning composition according to claims 1-2 characterised in that all particles have a particle size within the range of plus or minus 70% of the average particle size
- 4. Cleaning composition according to claim 3 characterized in that all particles have particle size within the range of \pm 50% of the average particle size.
- 5. Cleaning composition according to claims 1-4 characterised in that the particles have sphericity, such that the ratio between the longest and the shortest diameter of a particle in any one direction is at most 3:1
- 6. Cleaning composition according to claim 5 characterised in that the particles have a smooth round shape.

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- 7. Cleaning composition according to claims 1-6 characterised in that it has a viscosity of between 100 and 1000 mPas at 21 sec⁻¹.
- 8. Cleaning composition according to claims 1-7 characterised in that the liquid and the particles have different colours.
- 9. Cleaning composition according to claim 8 characterised in that the liquid and the abrasive particles have contrasting colours.
- 10. Cleaning composition according to claims 1-9 characterised in that it contains at least 0.1 but less than 15% surfactant.
- 11. Cleaning composition according to claims 1-10 characterised in that the surfactant is chosen from anionic surfactants, nonionic surfactants and mixtures thereof.
- 12. Cleaning composition according to claims 1-11 characterised in that it contains 0.1-20% of abrasive particles.
- 13. Process for cleaning a hard surface comprising the step of applying to the surface a cleaning composition according to any one of claims 1-12.



Inte al Application No

INTERNATIONAL SEARCH REPORT PCT7EP 01/11881 A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C11D17/00 C11E C11D3/14 C11D3/12 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 7 C11D Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X US 5 741 770 A (BLANDIAUX GENEVIEVE ET 1-13 AL) 21 April 1998 (1998-04-21) column 4, line 23-36 Υ 1 - 13column 8, line 61 -column 9, line 9 claims 1,6; example 1 X WO 97 41204 A (COLGATE PALMOLIVE CO) 1 - 136 November 1997 (1997-11-06) page 6, line 9-18 Υ 1 - 13page 7, line 15,16 page 16, line 11-21 page 19, line 13,14 claims 1,6 Further documents are listed in the continuation of box C. X Patent family members are listed in annex. Special categories of cited documents: *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the ad-"O" document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *&* document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 4 March 2002 12/03/2002 Name and mailing address of the ISA Authorized officer

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